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# COMPOSITION OF TRACE-MINERAL INCLUSIONS IN CASSITERITE FROM DATA FROM POINT X-RAY SPECTRAL ANALYSIS

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ABSTRACT. The use of point x-ray spectral microscopic analysis to study the composition of the trace-mineral impurities contained in cassiterite from the Etyka tin ore deposit is described. The results of chemical and qualitative x-ray analysis, as well as of microanalysis, are described. It is anticipated that further study of the composition of cassiterite will result in the discovery of an entire new series of unusual mineral impurities.

The special features of the chemical composition of cassiterite have long /214* attracted the attention of researchers because these features are at the base of the typogenic properties of this mineral and make it possible to answer questions concerned with the genesis of tin ore deposits with sufficient authenticity and, as a result, determine the practical significance of such deposits.

As is known, these questions have been discussed in the Soviet Union in papers by A.M. Bolyreva (1941), Ya.D. Gotman (1941), G.L. Vazbutskiy (1941), Iv. F. Grigor'yev and Ye. I. Dolmanova (1951), Ye. I. Dolmanova (1959), G.B. Zhilinsky (1955), and others.

The following trace-mineral impurities have been established as contained in the ore. This is the result of the study made by these researchers of cassiterites from various deposits of a variety of tin ore formations in crystals: tapiolite, wolframite, rutile, arsenopyrite, pyrite, zircon, quartz, clear mica (muscovite and zinnwaldite), and, with a lesser degree of certainty, hematite and magnetite. The sizes of these minerals differ, but only those visible in the conventional light microscope have been definitely proven.

In the majority of cases, the crystals of the colored trace-mineral impurities are so thin that they are translucent to chestnut, red, brown and yellow colors. This same coloring is observed in many zones of cassiterite in which no minerals can be seen under the microscope. This has led to the assumption that the minerals

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* Numbers in the margins indicate pagination in the foreign text.

occur in these colored zones, but are much smaller in size. This has been confirmed indirectly by the similar chemical compositions of the colored zones /215 (according to data from spectral analysis) and the zones with the mineral impurity inclusions. Some zones of the cassiterite show concentrations of several minerals. These zones have different colors in different sections, in different shades of the colors listed above, depending on the amount of impurity. There are cases of "superimposition" of individual shades on each other.

As a rule, the trace-mineral impurities are regularly located in zones of cassiterite crystal growth (Grigor'yev, Dolomanova, 1951; Dolomanova, 1959).

Many of the trace-mineral impurities remain undetermined because of their small size and the difficulties in diagnosing them by conventional methods.

The recently developed point x-ray spectral microscopic analysis method permits studying the composition of trace-mineral impurities more fully and accurately, even those measuring 1 to 2 microns.

We, for our purpose, selected a first generation black cassiterite from the Etyka deposit in the Transbaykal containing the largest amount of impurities.

The Etyka tin ore deposit is a cassiterite-feldspar-quartz formation as far as genetic features are concerned (Grigor'yev, Dolomanova, 1956). The ore-bearing veins occur in arenaceous-shale rocks of $J_1$ age. The veins are composed of quartz, amazonite topaz, zinnwaldite, cassiterite, with lesser amounts of albite, fluorite, wolframite, smirnovskite, arsenopyrite, pyrite, stannite, sphalerite, chalcopyrite, and galena, and other minerals.

Cassiterite is crystallized in the casings of the veins along with topaz and quartz, and at the same time there are occasional occurrences of radial aggregates of mixed cassiterite-topaz composition. The cassiterite sometimes branches out to the side from these elongated formations and intersects the topaz, but more often fills the interstices between its grains, together with first generation zinnwaldite and quartz. There are individual cases of the topaz filling the interstices between the cassiterite crystals. Cassiterite more often forms inclusions in the quartz, corroded by it and the amazonite. Cassiterite is found together with smirnovskite, but their age relationship is unclear, and it is only in rare cases that inclusions of cassiterite in the smirnovskite, or corrosion of the smirnovskite by the

smirnovskite by the cassiterite are seen. Zinnwaldite, pyrite, fluorite, second generation cassiterite, and other materials penetrate into the cracks in the cassiterite. Cassiterite can be corroded by sulfides.

The cassiterite aggregates are unevenly distributed in the vein. They form a continuous border at the casings, or are found in individual segregations, alternating with topaz, zinnwaldite and quartz. They are small, 1 to 2 cm in diameter, more often smaller. Occasionally, one finds individual, small (2 to 3 mm long) crystals featured by a simple external shape. They are a combination of a tetragonal prism and a pyramid, sometimes coalescing in polysynthetic twinning. Even smaller bipyramidal crystals of cassiterites are characteristic of the topaz greisens adjacent to the veins.

Cassiterite is represented by three generations, but first generation cassiterite prevails in the veins. It is black in color, with a metallic, or dull finish, and is friable.

Zonal structure and sharp fluctuations in trace-mineral impurities in /216
individual zones are quite characteristic of the cassiterite from the Etyka deposit. One zone will contain mostly impurities, in another they will be of minor importance, and in a third they will be more or less evenly divided with the cassiterite (Figure 1). Often seen are zones saturated with mineral impurities repeated in the cassiterite more than once, but there is no pattern to the manner of their repetition.

Individual zones in the cassiterite appear darker, or lighter, depending on the location and combination of the mineral impurities. Those zones, in which the sizes of the ore minerals are larger, also have a black color, in addition to chromatic colors. These zones are opaque. Cassiterite crystals also become opaque, black, when mineral impurities are high. The cassiterite is translucent to red, brown, or other colors in sections with impurities.

Sections of cassiterite containing large amounts of ore mineral impurities polish better and have greater reflectivity than do "purer" sections, those free of impurities.

The large content of various mineral impurities in the cassiterite make it very friable and porous, the result of loose intergrowth of the various trace-minerals with each other, and with the cassiterite. The specific gravity of black cassiterite is less than that of the light mineral.

Qualitative spectral analysis of cassiterite found Nb, Ta, Fe, Mn, W, Ti, Zr, Sc, Al, Si, As, Ga, V, Be, Pb, Cu, Ca, Mg, In.

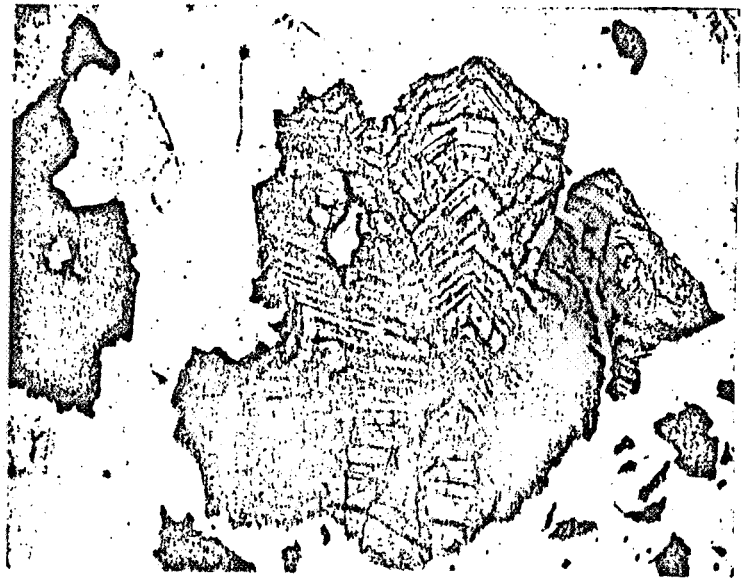


Figure 1. Zonal cassiterite from the Etyka deposit. (Microsection, one Nicol prism, magnification 10).

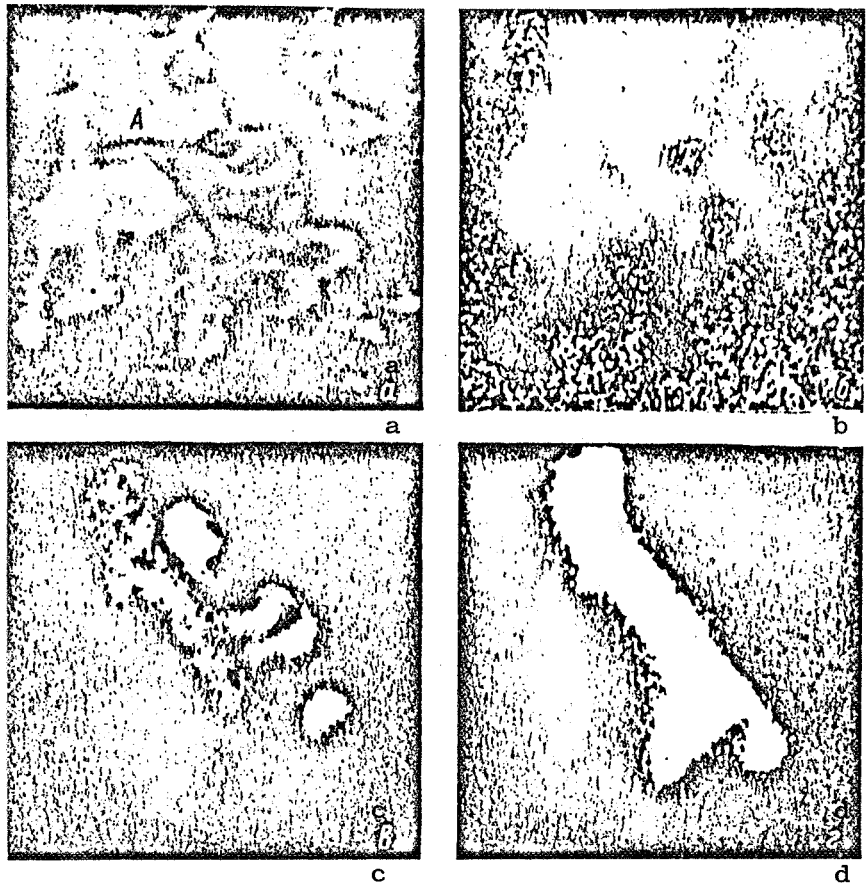



Figure 2. Distribution of elements in cassiterite.

a - image in absorbed electrons (coefficient of absorption of electrons higher the lower the atomic number. The light regions are sites containing the lighter elements, the dark those containing the heavier elements); b - image in $Sn_{L\alpha}$ rays; c - image in $Fe_{K\alpha}$ rays; d - image in $Ti_{K\alpha}$ rays; magnification 1000.

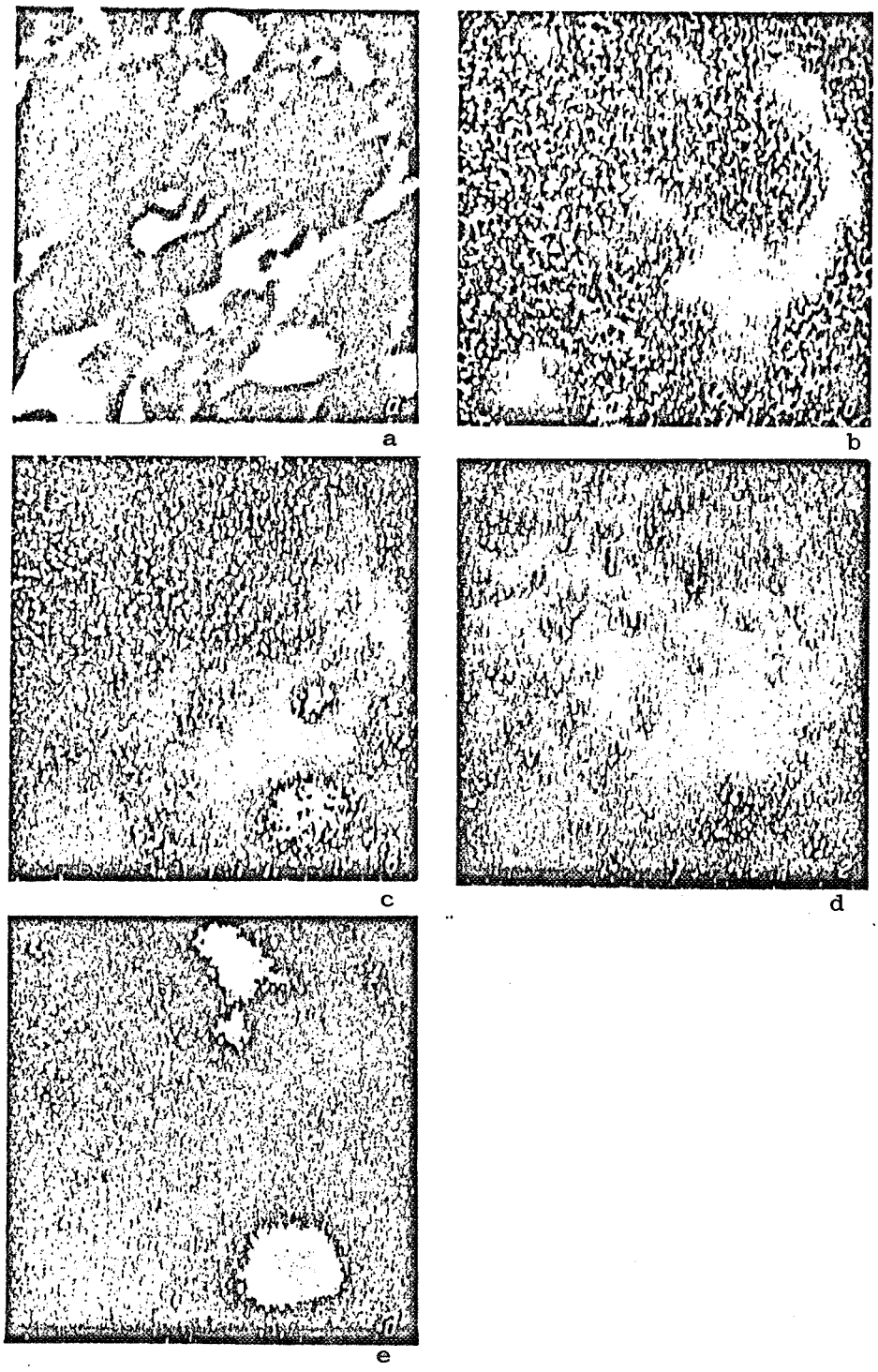



Figure 3. Distribution of elements in cassiterite.

a - image in absorbed electrons; b - image in $Sn_{L\alpha}$ rays; c - image in $Fe_{K\alpha}$ rays; d - image in $Nb_{L\alpha}$ rays; e - image in $Ti_{K\alpha}$ rays. Magnification 1000.

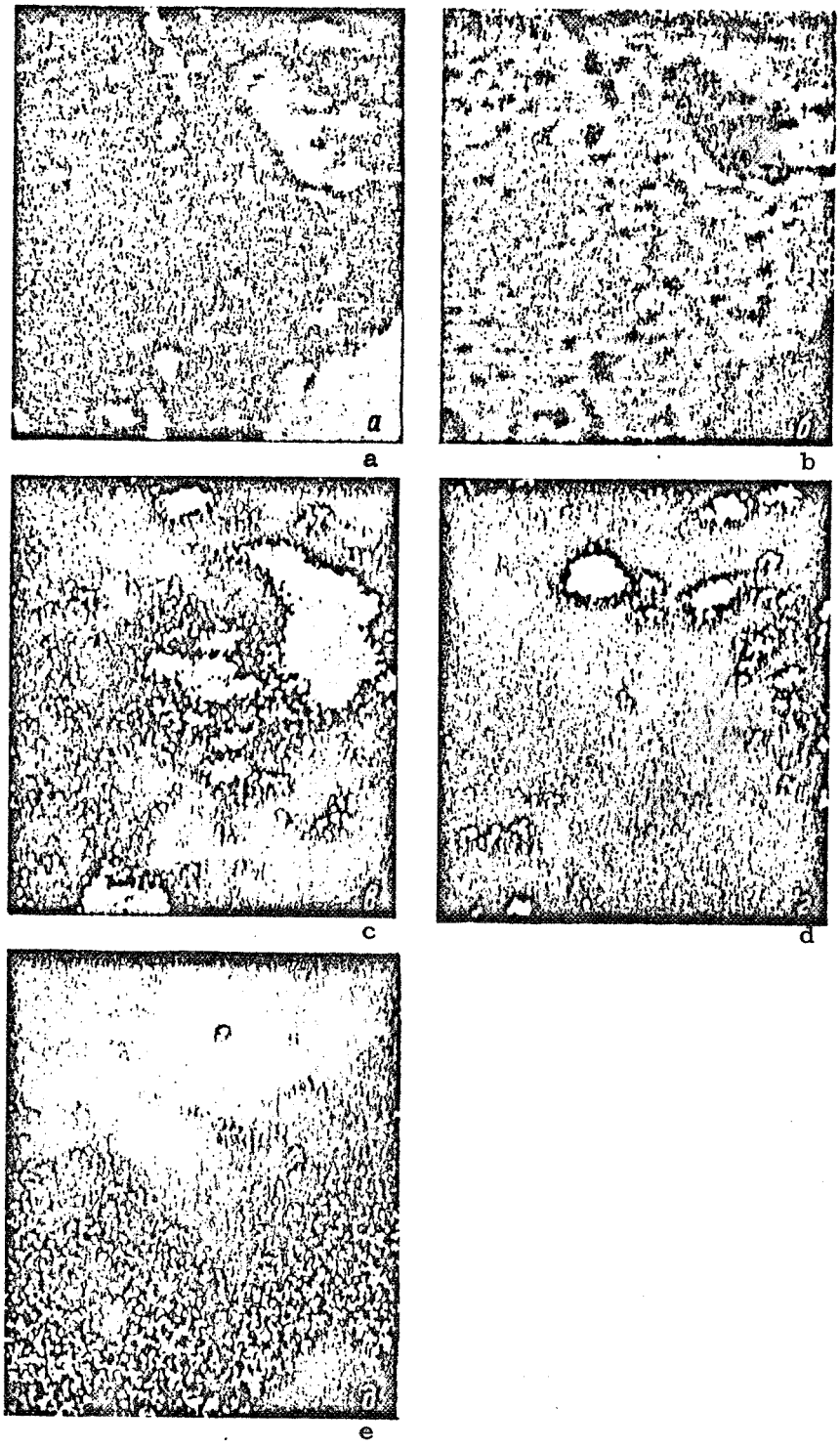



Figure 4. Distribution of elements in cassiterite.

a - image in absorbed electrons; b - image in absorbed electrons (inverted); c - image in $Fe_{K\alpha}$ rays; d - image in $Ti_{K\alpha}$ rays; e - image in $Sn_{L\alpha}$ rays. Magnification 500.

Figure 5. Intergrowth of tapiolite (1) and wolframite (2) in cassiterite (polished section 12/Er, magnification 450). Etyka deposit.

Chemical analysis of black cassiterite showed (in %): $SnO_2$ 93.52, $SiO_2$ 0.92, $TiO_2$ 0.87, $ZrO_2$ 0.54, $WO_3$ 0.60, $Fe_2O_3$ 0.38, $(Nb, Ta)_2O_5$ 1.04, MnO 0.84, $Al_2O_3$ 1.07, CaO 0.06, MgO 0.02; sum 99.86; specific gravity 6.547 (analyst M. O. Steppan).

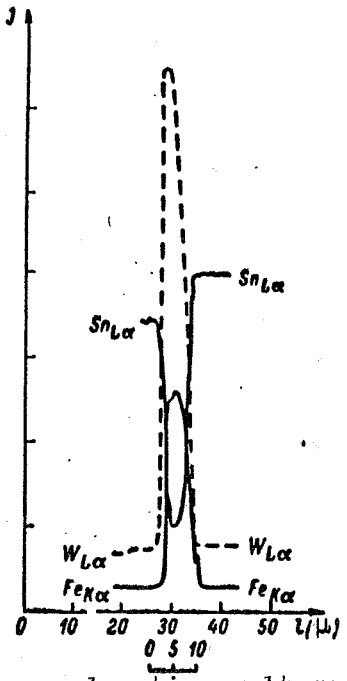
Qualitative X-ray chemical analysis of black cassiterite showed (in %): Zr 0.2, W 3, Nb 1, Ta 0.5 (analyst I. B. Borovskiy).

Microanalysis confirmed the presence in the cassiterite of certain of the above-listed trace-mineral impurities, wolframite and rutile, for example, and also detected new, previously unknown, or unproven, minerals. The presence of hematite (Figures 2c, 4c), ilmenite with an admixture of niobium (Figures 3a, b, c, d, e), and rutile (Figures 3e, 4d), was proven. Tight intergrowth of certain minerals was observed as well. Proof of this is the noncoincidence of the image in the $Fe_{K\alpha}$ and $Ti_{K\alpha}$ rays (Figure 2) and the results of the qualitative analysis at point A (Figure 2), where Fe = 52.5% and Ti = 19.4% (no correction made for fluorescent radiation).

If it is assumed that these elements are included in oxide compositions

(since there are no other elements at this point) we obtain $TiO_2$ 32.4%, $Fe_2O_3$ 68.9% (sum 101.3%).

It is possible that there are several minerals growing together at this site, rather than one.



accelerating voltage 30 kv

Figure 6. Change in the intensities of characteristic lines of the elements Fe, W, and Sn during scanning by an electron beam along the inclusion of the wolframite in cassiterite from the Etyka deposit.

Similar intergrowths between tapiolite and wolframite were observed under a light microscope (Figure 5) in this same cassiterite. It seems evident that these intergrowths of the various minerals and their inclusions in other minerals, are widely developed in nature. P. Ramdor (1962, p. 925), for example, notes that the hematite in the tin ore deposit at Pululus in Argentina "contains crumbled, minute bodies (smaller than 1 micron) that evidently are cassiterite with precisely the same shape as is customary for rutile."

The presence of wolframite was proven during the scanning of an inclusion of this mineral by an electron beam (Figure 6). The wolframite contains a good deal more iron than manganese. Of particular interest is the finding of the inclusion of corundum in the cassiterite, which, when irradiated by an electron beam, luminesced with the crimson color typical of ruby (Figures 7a, c, d). X-ray spectrography (Figure 8) confirmed the presence of this mineral.

In conclusion, it should be pointed out that /221 the impurities in the first generation black cassiterite from the Etyka deposit total 6.5%.

The greater part, if not all of the elements observed in cassiterites are included in the composition of the trace-minerals - wolframite, tapiolite, rutile, ilmenite, chromite, ruby, corundum, hematite, quartz, zinnwaldite, zircon. The question of the mineral form in which copper chloride is present is an open one.

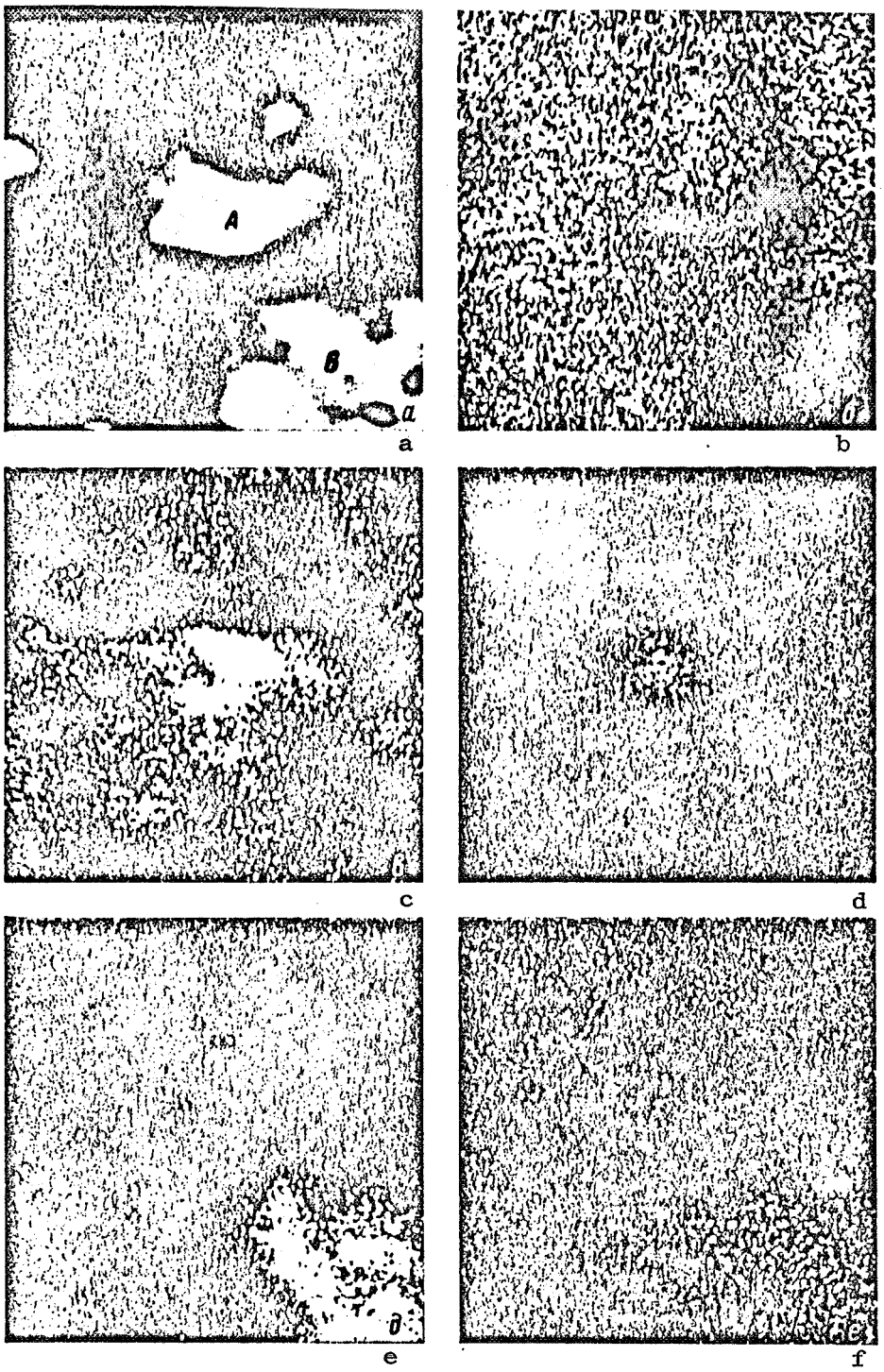
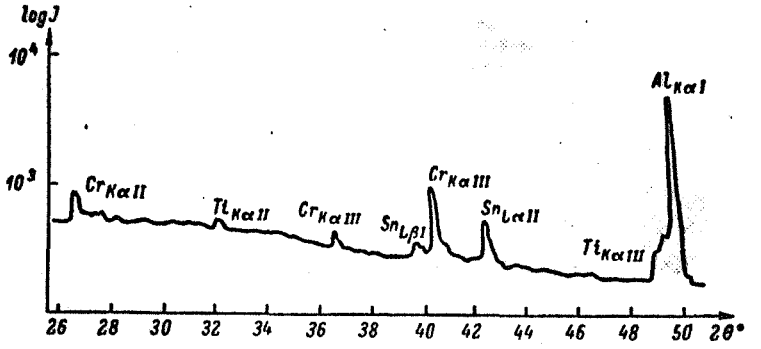



Figure 7. Distribution of elements in cassiterite.

a - image in absorbed electrons (A - corundum inclusion; B - mineral containing Cu and Cl); b - image in $Sn_{L\alpha}$ rays; c - image in $Cr_{K\alpha}$ rays; d - image in $Al_{K\alpha}$ rays; e - image in $Cu_{K\alpha}$ rays; f - image in $Cl_{L\alpha}$ rays. Because of low sensitivity of instrument to $Al_{K\alpha}$ and $Cl_{K\alpha}$ radiation, their images are not as bright as the $Cr_{K\alpha}$ and $Cu_{K\alpha}$ images. Magnification 1000.




Accelerating voltage 30 kv
Analyzing crystal - mica

Figure 8. X-ray spectrogram of the inclusion of corundum in the cassiterite from the Etyka deposit (see Figure 7).

The copper chloride retained in the cassiterite suggests that the chlorine too takes part in the mineral formation, but the role it plays is unclear because of the high degree of solubility of chlorides. They are retained only under special conditions, in the form of trace-minerals in gas-liquid inclusions, and as has been established, in the form of trace-minerals in cassiterite growth zones.

Further study of the composition of cassiterite, as well as of other minerals, evidently will make it possible to find a whole new series of unusual mineral impurities. Research of this nature is extremely important for an understanding of the processes of mineral formation in nature.

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